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(54) Title: <b>DISHWASHER DETERGENT AND USE THEREOF</b>			
(57) Abstract			
<p>A liquid, aqueous dishwasher detergent has a pH value of 6-9, preferably 6-8, and contains: an enzyme belonging to the group amylase, protease and lipase, or a mixture thereof; and a non-ionic surfactant having an instant foaming ability below 120 mm, measured according to the Ross-Miles ASTM D 1173-53. In one embodiment, the dishwasher detergent is enclosed in a water-dispersible or water-soluble capsule.</p>			

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## DISHWASHER DETERGENT AND USE THEREOF

This invention relates to a dishwasher detergent having a pH value of 6-9 and preferably being enclosed in a 5 water-soluble or water-dispersible capsule. The inventive detergent has been found to have excellent properties when used as a dishwasher detergent, despite it being neutral or only weakly alkaline.

To prevent excessive foaming, dishwasher detergents 10 have to be low-foaming and therefore only contain small amounts of surfactants. In order to achieve a sufficient cleaning power, it has therefore been necessary to incorporate, in the dishwasher detergents, large amounts of alkaline agents, such as sodium silicates, sodium carbonates, sodium tetraborates and sodium hydroxide, or mixtures thereof, as well as bleaching chemicals, such as chlorine isocyanurates. The ready-to-use solutions of the 15 dishwasher detergents therefore become strongly alkaline, usually having a pH value above 9, preferably above 11. 20 When diluted, these detergents have a skin-irritant effect and are even corrosive in many cases. Further, high alkalinity results in corrosion of the dishes. It is therefore desirable to reduce the alkalinity of the dishwasher detergent while at the same time maintaining its cleaning 25 power.

It has now been found possible to formulate a dishwasher detergent that does not contain any alkaline agents, or but small amounts thereof, and has excellent cleaning power. The inventive dishwasher detergent is 30 liquid and aqueous, has, when in concentrated form, a pH value of 6-9, preferably 6-8, and contains a) an enzyme belonging to the group amylase, protease and lipase, or a mixture thereof, and b) a non-ionic surfactant having an instant foaming 35 ability of less than 120 mm, measured according to Ross-Miles ASTM D 1173-53.

By "surfactant" is meant a compound that, in a content of 0.1% by weight in water at 25°C, reduces the surface tension of the water to below 50 mN/m according to du Noüy. Preferably, the non-ionic surfactant gives a 5 surface tension below 30 mN/m. The inventive dishwasher detergent is suitably free from anionic and cationic surfactants.

In a special embodiment, the liquid dishwasher detergent according to the invention is enclosed in a water- 10 soluble or water-dispersible capsule. In this embodiment, the dishwasher detergent has a free water content of 2-18% by weight, preferably 3-15% by weight. Chemically-bonded water, such as hydrate water, is not included in the water contents indicated above. The presence of such a limited 15 amount of water makes it possible to stabilise the enzymes sufficiently to enable encapsulation, as well as to prevent the detergent from dissolving or dispersing the capsule when stored. It has further been found that the enzymatic activity in the encapsulated dishwasher detergent 20 is maintained at a high level also during storage for long periods of time. The encapsulation prevents direct contact with the detergent and makes it easy to avoid overdosage.

It is previously known to enclose detergent compositions in microcapsules or larger capsules consisting of a 25 water-soluble or water-dispersible casing of e.g. gelatin in order to protect and stabilise the components of the detergent and/or to facilitate dosage. Thus, DE 25 32 556 teaches how to enclose a water-free paste-like stain remover containing dispersed  $\text{SiO}_2$  particles. EP 261 754 30 teaches a soft elastic gelatin capsule enclosing a bubble bath composition that contains an amine salt of a long-chain alkyl ether sulphate, polyethylene glycol and glycerol. EP 339 307 discloses a washing detergent consisting of an encapsulated liquid detergent composition that contains a water-free organic solvent and a solid material 35 dispersed in the water-free organic solvent. The dispersed material is a complexing agent, such as zeolite or sodium

tripolyphosphate. However, none of the above specifications discloses a dishwasher detergent in accordance with the present invention. Neither does it appear from these specifications how to formulate a dishwasher detergent without using high contents of alkaline agents.

The enzymes to be included in the dishwasher detergent according to the invention are chosen according to the composition of the dirt to be removed. This means that if the dirt consists of protein, the enzyme component can basically consist of one protease only, whereas if the dirt is composed of several different types, such as fat, protein and polysaccharides, use is conveniently made of an enzyme mixture where the enzyme components are especially selected in view of the degradation of these substances. The enzymes are added in amounts providing effective cleaning, which generally means that the enzyme component makes up 4-25% by weight of the detergent, excluding free water. Examples of suitable enzymes are endoproteases, e.g. of serine type, which inter alia degrade egg residues. As amylase, one may choose an  $\alpha$ -amylase which hydrolyses 1,4-alpha-glycoside bonds to amylose and amylopectin and which therefore degrades gelatinised starch into water-soluble dextrans and oligosaccharides. Amylases are especially suitable for removing stains of pasta, chocolate and other types of starch. Lipases hydrolyse triglycerides in mono- and diglycerides, glycerol and fatty acids and are added to remove, inter alia, frying fat, oil, salad dressing and butter. Specific examples of enzymes are Alkalase 2.5 L, Type DX; Durazym 16.0 L, Type DX; Esperase 8 L, Type A; Savinase 8.0 L, Type A; Savinase 16.0 L, Type DX; Savinase 16.0 L, Type EX; Termamyl 300 L, Type DX; and Lipolase 100 L, Type EX; all sold by Novo Nordisk A/S, Denmark.

The non-ionic surfactant forming part of the dish-washer detergent has an instant foaming ability below 120 mm, measured according to Ross-Miles ASTM D 1173-53. Conveniently, one chooses a non-ionic surfactant having

an instant foaming ability of 20-120 mm, in which case an antifoaming agent should be added in order to reduce the foaming of the liquid dishwasher detergent. If the dishwasher detergent does not contain any antifoaming agent, a surfactant having an instant foaming ability below 20 mm is preferably used. Convenient low-foaming surfactants include hydroxyl compounds, such as alcohols that have been ethoxylated or alkoxyolated with an alkylene oxide having 3-4 carbon atoms and ethylene oxide. Preferably, the alkoxylates have a turbidity point below the use temperature of the detergent, most preferably 20-30° below this temperature. When preparing the alkoxylates, use is conveniently made of alcohols having 6-14 carbon atoms, preferably 8-11 carbon atoms. The number of ethyleneoxy groups suitably is 3-8, and the number of alkyleneoxy groups having 3-4 carbon atoms normally is 0-3 per hydrophobic group. In a preferred embodiment, the alcohol is first ethoxylated and then alkoxyolated with an alkylene oxide having 3-4 carbon atoms. Such compounds can be illustrated by the formula  $RO(C_2H_4O)_x(B)_yH$ , wherein R is a hydrocarbon group having 6-14 carbon atoms, preferably 6-11 carbon atoms, B is an alkyleneoxy group having 3-4 carbon atoms, x is 2-8, and y is 1-3. Preferably, the hydrocarbon group R is an aliphatic group, such as an alkyl group. Other non-ionic compounds that may be used in accordance with the invention are alkyl glycosides having a degree of polymerisation of 1-4, preferably 1-2, and alkyl glucamides, such as alkyl-N-methyl glucamide. The alkyl group usually contains 6-14 carbon atoms, preferably 6-11 carbon atoms. Other suitable non-ionic surfactants are block polymers of ethylene oxide and alkylene oxide having 3-4 carbon atoms. Examples of suitable alkyl groups of the non-ionic surfactants in accordance with the invention are 2-ethyl hexyl, octyl, n-decyl, dodecyl and straight or branched  $C_9-C_{11}$  alkyl groups. The low-foaming non-ionic surfactants according to the invention make up

5-95% by weight of the dishwasher detergent, preferably 15-75% by weight, excluding free water.

Preferably, the water-soluble or water-dispersible casing consists of a conventional soft and elastic capsule, usually having a volume of 1-10 ml, preferably a volume of 2-5 ml. The capsule shell may be based on gelatin, polyvinyl alcohol, polyethylene glycol, cellulose ethers, alginic acid or pectinic acid, and may further contain additives adjusting its elasticity and water solubility. Preferably, the capsule shell consists of a conventional composition containing gelatin, water and a plasticiser, such as glycol, glycerol or sorbitol. The detergent may be encapsulated by conventional methods, e.g. by using conventional apparatus with rotating drums.

15 The inventive dishwasher detergent may also contain e.g. antifoaming agents, solubilisers, stabilisers and scents. The antifoaming agents are preferably polar and water-soluble or water-dispersible, and usually serve to reduce the foaming caused by the non-ionic surfactant.

20 In addition to their antifoaming effect, the antifoaming agents have a certain cleaning and/or solubilising capacity. The amount of the antifoaming agents is 0-60% by weight of the dishwasher detergent, preferably 5-40% by weight, excluding free water. Examples of suitable

25 antifoaming agents are  $C_{1-4}$  alkyl esters of carboxylic acids having 8-16 carbon atoms, such as methyl laurate and ethyl laurate; tri- $C_{6-14}$  alkyl phosphate, such as trioctyl phosphate, tridecyl phosphate and trilauryl phosphate; and alcohols having 6-12 carbon atoms. The solubilisers, which

30 usually make up 0-30% by weight of the detergent, preferably 2-25% by weight, excluding free water, may be diols having 2-8 carbon atoms, such as 1,2-propanediol, 1,2-butanediol, 2,3-butanediol; glycerol; polyglycols, such as dipropylene glycol and tripropanediol; or ether gly-

35 cols, such as butyldiethylene glycol.

The invention will now be further illustrated by the following Examples.

**Examples 1-4**

5 A dishwasher detergent was formulated by adding an enzyme mixture consisting of

5 parts by weight of Alkalase 2.0 L, Type DX

5 parts by weight of Savinase 8.0 L, Type A

5 parts by weight of Lipolase 100 L, Type EX

10 10 parts by weight of Termamyl 300 L, Type DX

to a detergent solution consisting of

62 parts by weight of Ethoxilate, C<sub>11</sub> alcohol

(Dubanol 1) + 5 EO; Foaming 70 mm (instant) Ross-Miles;

Surface tension 29 mN/m

15 44 parts by weight of Methyl laurate

19 parts by weight of Butyldiethylene glycol.

The enzyme mixture contained about 50% by weight of free water, and the liquid dishwasher detergent thus came to contain about 8% by weight of free water.

20 Test plates with depressions containing peroxidase-labelled protein were washed according to the Eliza method, while lacquered metal sheets smeared with radioactively-labelled fat were washed at about 55-60°C in a Terg-O-Tometer machine. The detergent solution used in the

25 two tests had been obtained by dissolving a gelatin capsule containing 5 ml, 3 ml or 2 ml of the liquid dishwasher detergent, or 3 ml of the liquid dishwasher detergent, in 6 l of water. In the Terg-O-Tometer machine, 1 l of the detergent solution was used. After washing, the 30 remaining amounts of protein and fat were measured by the Eliza method and by measurement of the radioactivity, respectively. The following results were obtained.

Example	Detergent ml	Dirt removed	
		Fat, %	Protein, %
5	1	5	78
	2	2	78
	3	3	84
	4	3	90
10	(no gelatin capsule)		

It is evident from the results that both the fat and the protein were efficiently removed.

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**Examples 5-9**

A dishwasher detergent was formulated by adding an enzyme mixture consisting of

5 parts by weight of Alkalase 2.5 L, Type DX

20 5 parts by weight of Savinase 8.0 L, Type A

10 parts by weight of Termamyl 300 L, Type DX

to a detergent solution made up of the following components:

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Example	Parts by weight	Component
5	50 35 15	C <sub>11</sub> alcohol (Dubanol 11) + 5 EO Ross-Miles 70 mm; Surface tension 29 mN/m Methyl laurate Butyldiethylene glycol
6	60 40	Octyl glycoside Ross-Miles 65 mm; Surface tension 35 mN/m Polyethylene glycol
7	66 17 7 10	Coco fatty alcohol + 7 EO + 1 PO Ross-Miles 90 mm; Surface tension 31.5 mN/m Methyl laurate Butyldiethylene glycol Water
8	100	C <sub>9-11</sub> alcohol + 4 EO Ross-Miles 20 mm; Surface tension 31 mN/m
9	100	Block polymer (Propylene glycol MV 1200 + 5 EO) Ross-Miles 5 mm; Surface tension 41 mN/m
A	55 45	Potassium decyl phosphate ester Water
B	100	The sodium salt of tall fatty acid

Test plates with depressions containing peroxidase-labelled protein were washed as in Examples 1-4. The dish-washer detergent solution was obtained by dissolving a gelatin capsule containing 3 ml of any of the above dish-washer detergent formulations in 6 l of water. After washing, the remaining protein was measured by the Eliza method. The following results were obtained.

Example	Washed-away protein in %
5	99
6	97
7	98
8	96
9	96
A	1
B	82

It is evident from the results that the inventive dishwasher detergents, i.e. Examples 5-9, are superior to the detergents of comparative Examples A and B.

20           **Example 10**

The dishwasher detergent according to Example 3 was compared with five commercial detergents, all containing considerable amounts of alkali. The commercial detergents were added in an amount of 5 g per 1 l of water. It was 25 proceeded as in Examples 1-4. The following results were obtained:

Detergent	Alkalinity	Form	Washed-away	
			Protein, %	Fat, %
Example 3	about 7	Capsule	94	86
Comparison C	about 12.5	Powder	83	95
Comparison D	about 12	Powder	87	73
Comparison E	about 12	Powder	82	72
Comparison F	about 12	Powder	82	74
Comparison G	about 11	Liquid	81	44

It is evident from the results that the inventive detergent had at least the same cleaning effect as commercial products C-G, in spite of the low dosage. It was especially efficient in washing away protein.

## CLAIMS

1. A liquid, aqueous dishwasher detergent, **c h a r -**  
5 **a c t e r i s e d** in that it has, when in concentrated  
form, a pH value of 6-9 and contains:
  - a) an enzyme belonging to the group amylase, protease  
and lipase, or a mixture thereof, and
  - b) a non-ionic surfactant having an instant foaming  
10 ability of less than 120 mm, measured according to Ross-  
Miles ASTM D 1173-53.
2. A dishwasher detergent as claimed in claim 1,  
**c h a r a c t e r i s e d** in that it contains a non-ionic  
15 surfactant having a foaming ability of 20-120 mm, as well  
as an antifoaming agent.
3. A dishwasher detergent as claimed in claim 1,  
**c h a r a c t e r i s e d** in that it contains a non-ionic  
20 surfactant having a foaming ability of less than 20 mm.
4. A dishwasher detergent as claimed in any one of  
claims 1-3, **c h a r a c t e r i s e d** in that the non-  
ionic surfactant is an alkoxylate in which an alcohol  
25 having 6-14 carbon atoms, preferably 8-11 carbon atoms,  
has been ethoxylated or alkoxyolated with an alkylene oxide  
having 3-4 carbon atoms and ethylene oxide.
5. A dishwasher detergent as claimed in any one of  
30 claims 1-4, **c h a r a c t e r i s e d** in that it con-  
tains a solubiliser.
6. A dishwasher detergent as claimed in any one of  
claims 1-5, **c h a r a c t e r i s e d** in that the enzyme  
35 component containing protease, amylase and/or lipase makes  
up 4-25% by weight of the detergent, excluding free water,

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the non-ionic surfactant makes up 5-95% by weight of the detergent, excluding free water, the antifoaming agent makes up 0-60% by weight of the detergent, excluding free water, and the solubiliser makes up 0-30% by weight,

5 excluding free water.

7. A dishwasher detergent as claimed in any one of claims 1-6, characterised in that it contains 2-18% by weight, preferably 3-15% by weight, of free water, chemically-bonded water being not included.

8. A dishwasher detergent as claimed in any one of claims 1-7, characterised in that it is enclosed in a water-soluble or water-dispersible capsule.

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9. A dishwasher detergent as claimed in claim 8,  
characterised in that the encapsulated amount  
is 1-10 ml.

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20 10. A dishwasher detergent as claimed in claim 8 or 9,  
characterised in that the capsule shell consists of a gelatin composition containing glycol, glycerol and/or sorbitol as plasticiser.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 93/01059

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C11D 3/386, C11D 1/72, C11D 1/722, C11D 17/08  
 According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE, A1, 2727463 (THE PROCTER & GAMBLE CO.), 5 January 1978 (05.01.78), page 10, line 29 - page 11, line 2, page 17, line 12 - page 19, line 1-27, claims 1,4,15  --	1-7
X	US, A, 4162987 (MAGUIRE, JR. ET AL.), 31 July 1979 (31.07.79), column 6, line 56, claims 1-2  --	1-10
P,A	EP, A2, 0554943 (UNILEVER N.V.), 11 August 1993 (11.08.93)  --	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	DE, A1, 4205071 (HENKEL KGAA), 26 August 1993 (26.08.93) -- -----	1-10

## INTERNATIONAL SEARCH REPORT

Information on patent family members

26/02/94

International application No.

PCT/SE 93/01059

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A1- 2727463	05/01/78	BE-A-	856068	27/12/77
		FR-A,B-	2355908	20/01/78
		GB-A-	1576946	15/10/80
		NL-A-	7706942	28/12/77
		US-A-	4162987	31/07/79
US-A- 4162987	31/07/79	BE-A-	856068	27/12/77
		DE-A-	2727463	05/01/78
		FR-A,B-	2355908	20/01/78
		GB-A-	1576946	15/10/80
		NL-A-	7706942	28/12/77
EP-A2- 0554943	11/08/93	CA-A-	2088230	04/08/93
DE-A1- 4205071	26/08/93	WO-A-	9317089	02/09/93

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